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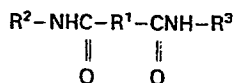
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(54) Polyphenylene ether compositions having improved processability.

(57) A polyphenylene ether composition comprises polyphenylene ether, optionally styrene resin, and a diamide represented by the formula



wherein R¹ is a C₁₋₁₀ linear or branched saturated or unsaturated aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue, an aromatic hydrocarbon residue, or such a residue having one or more substituents; and R² and R³, which may be the same or different, are each a C₁₋₁₀ linear or branched saturated or unsaturated aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue or an aromatic hydrocarbon residue, or such a residue having one or more substituents.

The composition has improved processability, due to high flowability, with a minimum decrease in heat resistance.

POLYPHENYLENE ETHER COMPOSITIONS HAVING IMPROVED
PROCESSABILITY

This invention relates to polyphenylene ether
5 compositions having improved processability.

Polyphenylene ether is a noteworthy engineering
plastics material which is very useful on account of
its outstanding electrical and mechanical properties,
high heat distortion temperature, and self-extinguishing
10 properties. On the other hand, it has some disadvantages.
It is slightly brittle due to low impact resistance.
It has a high melting point and a high melt viscosity,
and therefore requires a high molding temperature
and pressure. This leads to difficulty in
15 its melt processing.

In order to improve the processability of poly-
phenylene ether, resin blending has been proposed.
For example, Japanese Patent Publication No. 17812/1967
discloses blending a polyphenylene ether with high-
20 impact polystyrene resin. The composition obtained by
blending is improved in processability and impact

- 2 -

resistance, but the improvement in processability is not satisfactory.

There have been proposed ways of improving the processability of polyphenylene ether by adding a plasticizer.

For example, according to Japanese Patent Publication No. 5220/1974, the processability of polyphenylene ether is improved by incorporating in a polyphenylene ether or a composition of polyphenylene ether and styrene resin a compound selected from aromatic organic acid esters, polyesters having aromatic groups, organic phosphoric esters having aromatic groups, and chlorinated aromatic hydrocarbons which are highly miscible with polyphenylene ether resin.

When incorporating a plasticizer such as organic phosphate ester having aromatic groups, the polyphenylene ether or composition of polyphenylene ether and styrene resin is improved in processability but becomes extremely poor in thermal properties. This is attributable to the fact that the incorporated plasticizer disperses very uniformly into the matrix of the polyphenylene or composition of polyphenylene ether and styrene resin, lowering the glass transition point (T_g) of the matrix and consequently decreasing its heat resistance.

We postulated that the additive should have the following characteristics if the process-

- 3 -

ability (flowability) was to be improved without sacrificing the thermal performance (heat resistance).

1) It should be highly miscible with the matrix at the time of processing or when the system was in a flowable state, so that it produced the effect of improving flowability like a plasticizer.

2) It should separate from the matrix when the matrix was not flowing (at a temperature lower than the glass transition point of the matrix), so that it did not lower the T_g of the matrix: yet it should have a certain degree of miscibility with the matrix, so that it kept a certain level of interface bond strength and kept the mechanical strength even when it had separated from the matrix.

After extensive studies, we have concluded that an additive that satisfies the above two conditions simultaneously should have the following characteristics.

a) It should be a low-molecular weight compound having a constituent

unit which is miscible with the matrix (polyphenylene ether and styrene resin) and works as a plasticizer at the time of processing or when the system is in the flowable state.

b) It should crystallize and separate from the matrix phase at a temperature lower than the

- 4 -

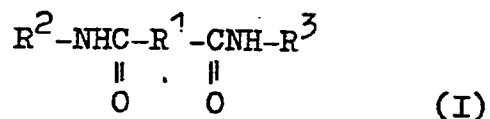
processing temperature (or the T_g of the matrix).

c) It should have a comparatively high polarity, so that crystallization occurs with certainty at a temperature lower than the processing temperature.

d) It should have a unit which has affinity for the matrix (polyphenylene ether and styrene resin) so that it maintains interface bond strength with the matrix even when it crystallizes and separates from the matrix phase.

According to the present invention the processability of a polyphenylene ether composition is improved by the incorporation of a diamide compound represented by the following general formula (I):

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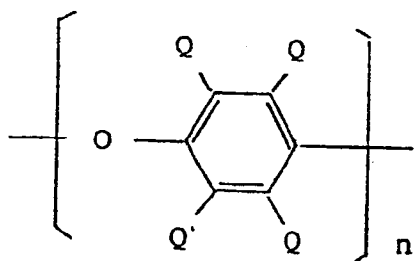
wherein R¹ is a C₁₋₁₀ linear or branched saturated or unsaturated aliphatic hydrocarbon residue, alicyclic

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- 5 -

hydrocarbon residue or aromatic hydrocarbon residue,
 or such a residue having one or more substituents; and
 R^2 and R^3 are each independently a C_{1-10} linear or
 5 branched saturated or unsaturated aliphatic hydrocarbon
 residue, alicyclic hydrocarbon residue or aromatic
 hydrocarbon residue or such a residue having one or
 more substituents.

The polyphenylene ether usable in this invention
 10 has a repeating structural unit represented by the
 following general formula (II):



(II)

- 6 -

where the ether oxygen atom in one unit is connected to the benzene nucleus of the adjacent unit; n is at least 50; and Q is a monovalent substituent group which is independently selected from

hydrogen, halogen, hydrocarbon groups containing no tertiary- α -carbon atom, halohydrocarbon groups having at least two carbon atoms between the halogen atom and the phenyl nucleus, and halohydrocarbon oxy groups having at least two carbon atoms between the halogen atom and the phenyl nucleus.

Typical examples of polyphenylene ether include poly(2,6-dimethyl-1,4-phenylene) ether, poly(2,6-diethyl-1,4-phenylene) ether, poly(2-methyl-6-ethyl-1,4-phenylene) ether, poly(2-methyl-6-propyl-1,4-phenylene) ether, poly(2,6-dipropyl-1,4-phenylene) ether, poly(2-ethyl-6-propyl-1,4-phenylene) ether, poly(2,6-dibutyl-1,4-phenylene) ether, poly(2,6-dipropenyl-1,4-phenylene) ether, poly(2,6-dilauryl-1,4-phenylene) ether, poly(2,6-diphenyl-1,4-phenylene) ether, poly(2,6-dimethoxy-1,4-phenylene) ether, poly(2,6-diethoxy-1,4-phenylene) ether, poly(2-methoxy-6-ethoxy-1,4-phenylene) ether, poly(2-ethyl-6-stearyloxy-1,4-phenylene) ether, poly(2,6-dichloro-1,4-phenylene) ether, poly(2-methyl-6-phenyl-1,4-phenylene) ether, poly(2,6-dibenzyl-1,4-phenylene) ether, poly(2-ethoxy-1,4-phenylene) ether, poly(2-chloro-1,4-phenylene)

- 7 -

ether, and poly(2,5-dibromo-1,4-phenylene) ether.

They also include a copolymer of 2,6-dimethylphenol and 2,3,6-trimethylphenol, a copolymer 5 of 2,6-dimethylphenol and 2,3,5,6-tetramethylphenol, and a copolymer of 2,6-diethylphenol and 2,3,6-trimethylphenol.

The polyphenylene ethers usable in this invention also include modified polyphenylene ethers produced by grafting 10 styrene monomer (such as styrene, p-methylstyrene, and α -methylstyrene) onto the polyphenylene defined by the above-mentioned formula.

The above-mentioned polyphenylene ethers can be produced by such known methods as disclosed in U.S. Patent 15 Nos. 3306874, 3306875, 3257357, and 3257358; Japanese Patent Publication No.17880/1977; and Japanese Patent Laid-open No. 51197/1975.

The groups of the polyphenylene ethers preferred for this invention include one which has an 20 alkyl substituent group at the two ortho positions with respect to the ether oxygen atom; a copolymer of 2,6-dialkylphenol and 2,3,6-trialkylphenol; and a graft polymer obtained by grafting styrene monomer onto the polyphenylene ether skeleton.

25 The styrene resins usable in this invention include

homopolymers such as polystyrene, poly- α -methylstyrene, and poly-p-methylstyrene; high-impact polystyrene modified with butadiene rubber, styrene-butadiene copolymer, 5 ethylene-propylene copolymer, or ethylene-propylene-diene terpolymer; and styrene-butadiene copolymer, styrene-maleic anhydride copolymer, styrene-acrylonitrile copolymer, styrene-acrylonitrile-butadiene copolymer, and styrene-methyl methacrylate copolymer. The styrene 10 resin is incorporated in an amount of 0 to 2,000 parts by weight, preferably 3 to 500 parts by weight, based on 100 parts by weight of polyphenylene ether resin.

The polyphenylene ether or the composition of polyphenylene ether and styrene resin may incorporate 15 one or more other polymers in order to improve impact resistance.

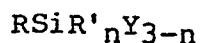
The polymers to be added are natural or synthetic rubbery polymers. They include, for example, natural rubber, polyisoprene, polybutadiene, styrene-butadiene 20 (block) copolymer, ethylene-propylene copolymer, and ethylene-propylene-nonconjugated diene terpolymer.

Polymers sensitized by the introduction of polar groups can also be used. Examples include the above-mentioned rubbery polymer when 25 sensitized and polyethylene, ethylene-vinyl

- 9 -

acetate copolymer, polypropylene, and other sensitized polyolefin.

The sensitivity can be imparted by grafting to the 5 above-mentioned polymer an unsaturated organic acid or an anhydride thereof (e.g., acrylic acid, methacrylic acid, itaconic acid, and anhydrides thereof) or an unsaturated silane compound (e.g., vinyltrimethoxysilane, vinyltriethoxysilane, vinyltriacetoxysilane, γ -meth- 10 acryloxypropyltrimethoxysilane, and propenyltrimethoxysilane) represented by the formula:



(where R is an ethylenic unsaturated hydrocarbyl or hydrocarbyloxy group; R' is an aliphatic saturated hydro- 15 carbyl group; Y is a hydrolyzable organic group; and n is 0, 1, or 2; and where there are two or three Y's, they may be the same or different), or by changing the above-mentioned graft-modified rubbery polymer or resinous polymer into an ionomer. (An ionomer is produced by 20 introducing metal ions into the part of the carboxyl groups connected to the graft chains of the polymer.)

The sensitized polymer can also be obtained by block- or random-polymerization of ethylene and vinyl monomer (such as an unsaturated organic acid 25 e.g., acrylic acid, and an ester thereof, having polar group) or vinyl silane.

The rubbery polymer or the polymer provided with sensitivity is incorporated in an amount of 0.5 to 50 wt%, preferably 2 to 4 wt%, based on the weight of the total polymer components.

In the cases where a sensitized polymer is used, it is preferable to add an inorganic filler. Where the sensitivity-provided polymer and an inorganic filler are used in combination with each other, a special structure is formed in which the sensitivity-provided polymer is dispersed in the polyphenylene ether or composition of polyphenylene ether and styrene resin and the inorganic filler is selectively filled into the sensitivity-provided polymer. Such a structure provides outstanding mechanical strength.

The inorganic filler is inorganic powder such as titanium oxide, zinc oxide, talc, clay, calcium carbonate, and silica which are known as fillers for synthetic resins.

The inorganic filler should have an average particle diameter of 0.05 to 1.0 micron. It is used in an amount of 0.5 to 60 wt%, preferably 1 to 45 wt%, based on the weight of the resulting composition.

Other polymers include polyphenylene ether-grafted polyolefin and polystyrene-grafted polyolefin.

25 The polyphenylene ether-grafted polyolefin can be obtained by grafting glycidylated polyphenylene ether

onto a polyolefin having carboxyl group or acid anhydride group on the main chain or side chain thereof.

The glycidylated polyphenylene ether can be obtained
5 by reacting polyphenylene ether with epichlorohydrin.

The polyolefin having carboxyl group or acid anhydride group on the main chain or side chain thereof include, for example, ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, maleic anhydride-
10 modified polypropylene, maleic anhydride-modified polyethylene, and maleic anhydride-modified ethylene-vinyl acetate copolymer.

The polyphenylene ether-grafted polyolefin can also be obtained by grafting polyphenylene ether onto a poly-
15 olefin having a glycidyl group on the side chain, such as ethylene-glycidyl methacrylate copolymer, and ethylene-vinyl acetate-glycidyl methacrylate copolymer.

The polyphenylene ether moiety of the graft polymer should preferably have a molecular weight of 5,000 to
20 100,000, and the number-average molecular weight of the polyolefin chain should be 100 to 100,000, preferably 3,000 to 50,000.

The polystyrene-grafted polyolefin can be obtained by grafting a styrene copolymer onto a polyolefin, said
25 styrene copolymer having a carboxylic acid group or a cyclic acid anhydride group on the main chain or side

- 12 -

chain of polystyrene, e.g., styrene-maleic anhydride copolymer, styrene-citraconic anhydride copolymer, styrene-itaconic anhydride copolymer, styrene-asconit
5 anhydride copolymer, styrene-acrylic acid copolymer, and styrene-methacrylic acid copolymer; and said polyolefin having a glycidyl group on the side chain, e.g., ethylene-glycidyl methacrylate copolymer and ethylene-vinyl acetate-glycidyl methacrylate copolymer.

10 The styrene copolymer having carboxyl group or cyclic acid anhydride group on the main chain or side chain, which is used for producing the polystyrene-grafted polyolefin in this invention, should preferably contain more than 50 wt% of styrene units and more than
15 3 wt% of carboxyl group units or cyclic acid anhydride units.

The polyolefin having a glycidyl group on the side chain, which is used for synthesis of the graft polymer, should have a number average molecular weight of 1,000
20 to 100,000, preferably 3,000 to 50,000.

The polyphenylene ether-grafted polyolefin is used in an amount of 0.1 to 50 wt%, preferably 1 to 30 wt%, and the polystyrene-grafted polyolefin is used in an amount of 1 to 80 wt%, preferably 1 to 30 wt%, based on
25 the total polymer such as the total weight of polyphenylene ether or a composition of polyphenylene ether and styrene resin, and polyphenylene

- 13 -

ether-grafted polyolefin and/or polystyrene-grafted polyolefin.

The grafted polyolefin may be added after graft
5 polymerization. In the case where a polyolefin having glycidyl groups is used, the grafting reaction can be accomplished by mixing it with polyphenylene ether or styrene resin having a carboxyl group or a carboxylic acid anhydride group at a high temperature above 150°C.

10 Thus, mixing a polyolefin containing glycidyl groups and polyphenylene ether or a composition of polyphenylene ether and styrene resin at a high temperature brings about the grafting reaction and provides a composition containing polyphenylene ether-grafted polyolefin and/or
15 polystyrene-grafted polyolefin. This method is preferable from an economical point of view.

The diamide compound of the general formula (I) will now be discussed.

Examples of R^1 in the general formula (I) include a methylene group, ethylene group, trimethylene group, propylene group, tetramethylene group, isobutylene group, pentamethylene group, cyclopentylene group, hexamethylene group, cyclohexylene group, octamethylene group, decamethylene group, and phenylene group.

Examples of R^2 and R^3 include a methyl group, ethers group, propyl group, isopropyl group, butyl group, isobutyl group, t-butyl group, pentyl group, isopentyl group, cyclopentyl group, hexyl group, isohexyl group, cyclohexyl group, heptyl group, octyl group, decyl group, and phenyl group.

15 R^1 , R^2 , and R^3 may have one or more substituents.

Examples of the substituents include:

- R^4 (R^4 : C_{1-8} hydrocarbon group)
- X (X: halogen such as Cl, Br, and F)
- OR^5 (R^5 : H or C_{1-8} hydrocarbon group)
- 20 - NR^6R^7 (R^6 , R^7 : H or C_{1-8} hydrocarbon group)
- $OCOR^8$ (R^8 : H or C_{1-8} hydrocarbon group)
- COOH or metal salt thereof or acid anhydride group

- 15 -

-SO₃H-NO₂

-NO

5 -CN

The diamide compound used in this invention is intended to be miscible with the matrix components when the composition is in the flowable state for processing; but it is also intended to crystallize and separate from the matrix components when the molded composition is in use. Therefore, the diamide compound used in this invention should have a melting point slightly lower than the processing temperature.

The processing temperature for the composition of this invention is established between the T_g of the matrix (temperature at which the composition starts to flow) and the temperature at which the composition starts to decompose.

The glass transition point (T_g) of the mixture of polyphenylene ether and styrene resin varies depending on its composition. It is 103°C in the case of a composition of polyphenylene ether (1 part) and high-impact polystyrene (99 parts). Therefore, the processing temperature for a composition of polyphenylene ether and styrene resin is usually higher than 103°C. Polyphenylene ether usually begins to decompose at about 350°C in the

- 16 -

air. Thus, the processing is usually carried out at 105°C to 350°C.

Accordingly, the diamide compound used in this invention should have a melting point higher than 105°C, preferably higher than 130°C, particularly 130°C to 350°C. A diamide having a melting point lower or higher than the above-mentioned limit may be used in the case where the processing temperature becomes lower or higher than the above-mentioned limit due to the addition of stabilizer or plasticizer. The diamide compound is added in an amount of 0.1 to 25 parts by weight, preferably 0.5 to 20 parts by weight, particularly 2 to 10 parts by weight, based on 100 parts by weight of total polymers.

The composition of this invention may incorporate other additives according to the intended end use.

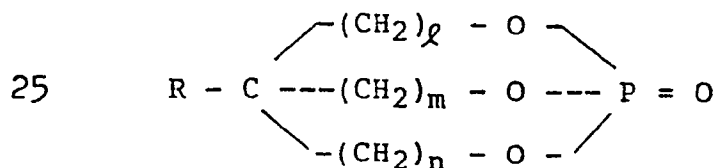
The additives include stabilizer, plasticizer, flame-retardant, inorganic filler, mold release, and colorant; and the polyphenylene ether compositions of this invention have improved flowability and are easy to process even when other additives are added.

Those additives which are most commonly used for the polyphenylene ether compositions of this invention are

- 17 -

stabilizers, colorants, and flame-retardants. Popular flame-retardants include, for example, phosphoric esters such as trimethyl phosphate, triethyl phosphate, tri-
 5 propylphosphate, tributyl phosphate, tripentyl phosphate, trihexyl phosphate, triphenyl phosphate, tricresyl phosphate, trixylenyl phosphate, tris(chloroethyl) phosphate, tris(dichloroethyl) phosphate, tris(bromoethyl) phosphate, tris(dibromoethyl) phosphate, tris(chlorophenyl)
 10 phosphate, tris(dichlorophenyl) phosphate, tris(bromophenyl) phosphate, and tris(dibromophenyl) phosphate; halogenated aromatic derivatives such as hexabromobenzene, pentabromotoluene, and decabromobiphenyl; antimony compounds such as triphenylantimony, tris(bromophenyl)-
 15 antimony, tris(dibromophenyl)antimony, and antimony oxide; and halides such as halogenated diphenyl carbonate, halogenated cyclodecane, halogenated phthalic acid anhydride, and halogenated polystyrene.

The polyphenylene ether composition is improved in
 20 both flame retardancy and heat resistance when the above-mentioned flame-retardant is used in combination with a bicyclopophosphate ester represented by the following general formula:



- 18 -

where ℓ is an integer of 0 to 2; m is an integer of 1 to 3; n is an integer of 1 to 3; and R is hydrogen or a C₁₋₁₉ alkyl group or derivative thereof.

5 Examples of this compound include 2,6-trioxano-1-phosphobicyclo[2,2,2]octane-1-oxide, 2,6,7-trioxano-1-phosphobicyclo[2,2,2]octane-4-methyl-1-oxide, and 2,6,7-trioxano-1-phosphobicyclo[2,2,2]octane-4-hexadecyl-1-oxide.

10 These flame retardants may be used individually or in combination with one another.

The invention is now described in more detail with reference to the following Examples and Comparative Examples.

15 EXAMPLE 1 and COMPARATIVE EXAMPLE 1

The following components were melted and mixed at 260°C for 7.5 minutes by using a Brabender.

50 parts by weight of poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic viscosity of 0.50 measured
20 in chloroform at 25°C; made by Mitsubishi Petrochemical Co., Ltd.).

50 parts by weight of high-impact polystyrene (465D, a product of Asahi Dow Co., Ltd.).

5 parts by weight of N,N'-diphenyladipic acid diamide
25 (having a melting point of 235°C as measured with the melting point measuring apparatus MP-1 made by Yamato

- 19 -

Kagaku Co., Ltd.).

After mixing was complete, the melt index at 250°C under a load of 10 kg was measured, which indicates the processability (flowability) of the composition. The composition was press-formed into test pieces for measurement of heat distortion temperature under a load of 18.6 kg/cm².

In Comparative Example 1, the diamide was not used. The results are shown in Table 1 and Fig. 1 in which the melt index is plotted against the heat distortion temperature.

EXAMPLES 2 TO 5 AND COMPARATIVE EXAMPLES 2 TO 5

The same experiments as in Example 1 and Comparative Example 1 were carried out except the ratio of poly-2,6-dimethyl-1,4-phenylene ether to high-impact polystyrene was changed as follows:

70/30 (Example 2 and Comparative Example 2),
60/40 (Example 3 and Comparative Example 3),
40/60 (Example 4 and Comparative Example 4), and
30/70 (Example 5 and Comparative Example 5).

The results are shown in Table 1 and Fig. 1.

It is noted in Table 1 that the composition is remarkably improved in flowability by adding 5 parts of N,N'-diphenyladipic acid diamide.

Table 1

| Example No. | Polyphenylene ether (parts by weight) | High-impact polystyrene (parts by weight) | N,N'-diphenyl- adipic acid diamide (parts by weight) | Melt index (g/10 min) | Heat distor- tion temper- ature (°C) |
|------------------------------|---|---|--|--------------------------|--|
| Example No. 1 | 50 | 50 | 5 | 10 | 128 |
| No. 2 | 70 | 30 | 5 | 2.8 | 148 |
| No. 3 | 60 | 40 | 5 | 5.2 | 140 |
| No. 4 | 40 | 60 | 5 | 15.1 | 121 |
| No. 5 | 30 | 70 | 5 | 39.6 | 101 |
| Comparative Example No. 1 | 50 | 50 | - | 3.4 | 130 |
| No. 2 | 70 | 30 | - | 0.9 | 152 |
| No. 3 | 60 | 40 | - | 1.7 | 143 |
| No. 4 | 40 | 60 | - | 5.2 | 122 |
| No. 5 | 30 | 70 | - | 13 | 104 |

- 21 -

Line A obtained by plotting the data of Comparative Examples 1 to 5 indicates how the flowability (melt index) is related with the heat resistance (heat distortion temperature) when the ratio of poly-2,6-dimethyl-2,4-phenylene ether to high-impact polystyrene is changed continuously.

In other words, line A indicates that as the ratio of high-impact polystyrene is increased, the flowability (melt index) increases but the heat distortion temperature decreases.

On the other hand, line B obtained by plotting the data in Examples 1 to 5 lies above line A. This apparently indicates the effect of this invention.

15

EXAMPLES 6 to 13 and

COMPARATIVE EXAMPLES 6 to 10

In Examples 6 to 13, the same experiments as in Example 1 were carried out except the quantity of N,N'-diphenyladipic acid diamide was changed to 0.5, 1, 3, 8, 10, 12, 15, and 20 parts by weight. The results are shown in Table 2 and Fig. 2.

In Comparative Example 6 to 10, N,N'-diphenyladipic acid diamide was replaced by triphenyl phosphate in an amount of 2, 3, 5, 7, and 10 parts by weight. It is a plasticizer which is known to produce the effect of improving the flowability of polyphenylene ether or a

25

composition of polyphenylene ether and styrene resin. The results are shown in Table 2 and Fig. 2.

Fig. 2 is based on the data in Table 2. In Fig. 5 2, the flowability (melt index) is plotted against the heat resistance (heat distortion temperature). The superscripts indicate the quantity of N,N'-diphenyl adipic acid diamide or triphenyl phosphate added.

Triphenyl phosphate is a well-known flame retardant 10 as well as a plasticizer. As the addition of this compound is increased, the composition greatly improves in processability (flowability) but decreases in heat resistance (heat distortion temperature). See line C in Fig. 2.

On the other hand, line D in Fig. 2 indicates that 15 as N,N'-diphenyl adipic acid diamide is added more, the flowability is greatly improved with a minimum of decrease in heat resistance (heat distortion temperature).

- 23 -

Table 2

| <u>Example</u> | <u>N,N'-diphenyl- adipic acid diamide (parts by weight)</u> | <u>Triphenyl phosphate (parts by weight)</u> | <u>Melt index (g/10 min)</u> | <u>Heat dis- tortion tempera- ture (°C)</u> |
|------------------------|---|--|----------------------------------|---|
| No. 6 | 0.5 | - | 5.0 | 127 |
| 7 | 1 | - | 4.0 | 128 |
| 8 | 3 | - | 7.0 | 128 |
| 1 | 5 | - | 10 | 128 |
| 9 | 8 | - | 13 | 127 |
| 10 | 10 | - | 19 | 123 |
| 11 | 12 | - | 20 | 116 |
| 12 | 15 | - | 50 | 120 |
| 13 | 20 | - | 82 | 121 |
| Comparative Example | | | | |
| No. 1 | - | - | 3.4 | 130 |
| 6 | - | 2 | 6.3 | 122 |
| 7 | - | 3 | 9.0 | 117 |
| 8 | - | 5 | 13 | 112 |
| 9 | - | 7 | 18 | 109 |
| 10 | - | 10 | 25 | 105 |

[Polyphenylene ether/high-impact polystyrene = 50/50]

- 24 -

EXAMPLE 14

Example 1 was repeated except that N,N'-diphenyl-adipic acid diamide was replaced by 5 parts by weight
5 of N,N'-dihexyladipic acid diamide (having a melting point of 158°C as measured by MP-21 made by Yamato Kagaku Co., Ltd.). The results are shown in Table 3.

EXAMPLE 15

Example 1 was repeated except that N,N'-diphenyl-
10 adipic acid diamide was replaced by 5 parts by weight of N,N'-dihexylterephthalic acid diamide (having a melting point of 204°C as measured by MP-21 made by Yamato Kagaku Co., Ltd.). The results are shown in Table 3.

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EXAMPLE 16

Example 1 was repeated except that N,N'-diphenyl-adipic acid diamide was replaced by 5 parts by weight
of N,N'-dihexylsuccinic acid diamide (having a melting
point of 226°C as measured by MP-21 made by Yamato
20 Kagaku Co., Ltd.). The results are shown in Table 3.

EXAMPLE 17

Example 1 was repeated except that N,N'-diphenyl-adipic acid diamide was replaced by 5 parts by weight
of N,N'-dihexylsebacic acid diamide (having a melting
25 point of 196°C as measured by MP-21 made by Yamato
Kagaku Co., Ltd.). The results are shown in Table 3.

Table 3

| <u>Example</u> | <u>Name</u> | <u>Melting point (°C)</u> | <u>Quan- tity added (parts)</u> | <u>Melt index (g/10 min)</u> | <u>Heat dis- tortion tempera- ture (°C)</u> |
|-----------------------------|--|-----------------------------------|---|--|---|
| No. 14 | N,N'-dihexyladipic acid diamide | 158 | 5 | 13 | 126 |
| 15 | N,N'-dihexyltere- phthalic acid diamide | 204 | 5 | 12 | 127 |
| 16 | N,N'-diphenylsuccinic acid diamide | 226 | 5 | 11 | 127 |
| 17 | N,N'-dihexylsebacic acid diamide | 196 | 5 | 12 | 127 |
| Compar- ative Example | | | | | |
| No. 1 | none | - | - | 3.4 | 130 |
| 8 | Triphenyl phosphate | 49 | 5 | 13 | 112 |

- 26 -

EXAMPLE 18 and COMPARATIVE EXAMPLE 11

The following components were dry-blended by using a supermixer, and then mixed and pelletized at 340°C by using a twin-screw extruder (PCM-45ø) made by Ikegai Iron Works, Ltd.

60 parts by weight of poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic viscosity of 0.50 measured in chloroform at 25°C; made by Mitsubishi Petrochemical Co., Ltd.).

40 parts by weight of high-impact polystyrene (HT-76, a product of Mitsubish Monsanto Co., Ltd.).

5 parts by weight of N,N'-diphenylterephthalic acid diamide (having a melting point of 337°C as measured with the melting point measuring apparatus MP-21 made by Yamato Kagaku Co., Ltd.).

The resulting pellets were injection-molded at a temperature of 340°C under an injection pressure of 1000 kg/cm² by using an injection molding machine N-100 (made by The Japan Steel Works, Ltd.) to measure the flow distance in a spiral cavity, 2 mm thick and 8 mm wide. Test pieces for measuring heat distortion temperature were also formed by using the same injection molding machine as above.

In Comparative Example, the same experiments as in Example were carried out except that N,N'-diphenyltere-

- 27 -

phthalic acid diamide was not used. The results are shown in Table 4.

EXAMPLE 19

5 Example 18 was repeated except that N,N'-diphenyl-terephthalic acid diamide was replaced by N,N'-diphenyl-fumaric acid diamide (having a melting point of 314°C as measured with the melting point measuring apparatus MP-21 made by Yamato Kagaku Co., Ltd.). The results are
10 shown in Table 4.

Table 4

| | <u>Spiral flow distance (mm)</u> | <u>Heat distortion temperature (°C)</u> |
|---------------------------|--------------------------------------|---|
| Example 18 | 360 | 143 |
| 15 Example 19 | 410 | 141 |
| Comparative Example 11 | 210 | 144 |

EXAMPLES 20 to 26 and

COMPARATIVE EXAMPLES 12 to 14

20 The following components were dry-blended in the ratio shown in shown in Table 5 by using a supermixer, and then mixed and pelletized at 280°C by using a twin-screw extruder (PCM-45ø) made by Ikegai Iron Works, Ltd. Poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic
25 viscosity of 0.47 measured in chloroform at 30°C; made

by Mitsubishi Petrochemical Co., Ltd.).

Polystyrene (HF-77, a product of Mitsubish Monsanto Co., Ltd.),

- 5 Maleic anhydride-grafted ethylene-propylene copolymer (containing 1.5 wt% of maleic acid anhydride; made by Mitsubishi Petrochemical Co., Ltd.).

Styrene-butadiene copolymer (1502, a product of Japan Synthetic Rubber Co., Ltd.),

- 10 Precipitated calcium carbonate (having an average particle diameter of 0.2 micron), and
N,N'-diphenyladipic acid diamide.

- The resulting pellets were injection-molded at a temperature of 300°C under an injection pressure of
15 1100 kg/cm² by using an injection molding machine N-100 (made by The Japan Steel Works, Ltd.) to measure the flow distance in a spiral cavity, 2 mm thick and 8 mm wide... Test pieces for measuring heat distortion temperature were also formed by using the same injection
20 molding machine as above.

In Comparative Examples, the same experiments as in Examples were carried out except that N,N'-diphenyladipic acid diamide was not used. The results are shown in Table 5 and Fig.3.

- 25 In Fig. 3, the flowability (spiral flow distance) is plotted against the heat resistance (heat distortion

- 29 -

temperature) based on the data in Table 5. Curve E was obtained by plotting the data in Comparative Examples 12, 13, and 14 in which N,N'-diphenyladipic acid diamide was not used. In this case, the flowability of the composition can be changed by the mixing ratio of poly-2,6-dimethyl-1,4-phenylene ether and polystyrene, but its extent is limited. On the other hand, the curve is shifted rightward when N,N'-diphenyl adipic acid diamide is added. (Curve F for Examples 20 and 21; curve G for Examples 22 to 24; and curve H for Examples 25 and 26) This suggests that the composition of this invention is greatly improved in flowability with no loss of heat resistance.

Table 5

| Formulation (parts by weight) | E x a m p l e s | | | | | | | | | | Comparative Examples | | | |
|---|-----------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-------------------------|-----|-----|----|
| | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 12 | 13 | 14 | 12 | 13 | 14 | |
| Poly-2,6-dimethyl-1,4-phenylene ether | 57 | 48 | 64 | 52 | 45 | 56 | 43 | 53 | 48 | 39 | 53 | 48 | 39 | 1 |
| Polystyrene | 33 | 42 | 26 | 38 | 45 | 34 | 47 | 37 | 42 | 51 | 37 | 42 | 51 | 30 |
| Maleic anhydride grafted-ethylene-propylene copolymer | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 1 |
| Styrene-butadiene copolymer | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | |
| Calcium carbonate | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | |
| N,N'-diphenyladipic acid diamide | 5 | 5 | 7 | 7 | 7 | 10 | 10 | - | - | - | - | - | - | |
| <u>Performance</u> | | | | | | | | | | | | | | |
| Spiral flow distance (mm) | 228 | 296 | 221 | 308 | 386 | 326 | 458 | 162 | 190 | 242 | 162 | 190 | 242 | |
| Heat distortion temperature, 18.6 kg load (°C) | 117 | 109 | 122 | 113 | 107 | 115 | 106 | 121 | 115 | 107 | 121 | 115 | 107 | |

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- 31 -

EXAMPLES 27 and 28 andCOMPARATIVE EXAMPLES 15 and 16

The following components were uniformly blended in
5 the ratio shown in Table 6 by using a supermixer, and
then mixed for grafting at 280°C and pelletized by using
a twin-screw extruder (PCM-45ø) made by Ikegai Iron Works,
Ltd.

Poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic
10 viscosity of 0.48 as measured in chloroform at 30°C; made
by Mitsubishi Petrochemical Co., Ltd.),

Polystyrene (HF-77, a product of Mitsubish Monsanto Co.,
Ltd.),

Ethylene-vinyl acetate-glycidyl methacrylate copolymer
15 (MFR = 4, containing 5 wt% of vinyl acetate and 10 wt%
of glycidyl methacrylate; made by Mitsubishi Petrochemical
Co. Ltd.),

Sytyrene-maleic anhydride copolymer (containing 10 wt%
of maleic acid anhydride), made by Arcopolymer Co., Ltd.),
20 and

N,N'-diphenyladipic acid diamide.

The resulting pellets were injection-molded in the
same way as in Example 20 to measure the flow distance
(spiral flow) and heat distortion temperature.

25 In Comparative Examples, the same experiments as in
Examples were carried out except that N,N'-diphenyladipic

- 32 -

acid diamide was not used. The results are shown in Table 6 and Fig.4.

In Fig. 4, the flowability (spiral flow distance) is plotted against the heat resistance (heat distortion temperature) based on the data in Table 6. Curve I was obtained by plotting the data in Comparative Examples 15 and 16 in which N,N'-diphenyladipic acid diamide was not used, and curve J was obtained by plotting the data in Examples 27 and 28. These results suggest that the composition of this invention is greatly improved in flowability with no loss of heat resistance.

- 33 -

Table 6

| | <u>Examples</u> | | <u>Comparative Examples</u> | |
|---|-----------------|-----------|---------------------------------|-----------|
| | <u>27</u> | <u>28</u> | <u>15</u> | <u>16</u> |
| <u>Formulation</u> (parts by weight) | | | | |
| Poly-2,6-dimethyl-1,4-phenylene ether | 50 | 55 | 50 | 42 |
| Polystyrene | 40 | 35 | 40 | 48 |
| Ethylene-vinyl acetate glycidylmethacrylate copolymer | 10 | 10 | 10 | 10 |
| Styrene-maleic anhydride copolymer | 10 | 10 | 10 | 10 |
| N,N'-diphenyladipic acid diamide | 5 | 5 | - | - |
| <u>Performance</u> | | | | |
| Spiral flow distance (mm) | 296 | 232 | 162 | 250 |
| Heat distortion temperature, 18.6 kg. load. (°C) | 113 | 119 | 118 | 108 |

EXAMPLE 29 and COMPARATIVE EXAMPLE 17

- The following components were uniformly blended in the ratio shown in Table 7 by using a supermixer, and
- 5 then mixed at 280°C and pelletized by using a twin-screw extruder (PCM-45 ϕ) made by Ikegai Iron Works, Ltd. Poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic viscosity of 0.47 measured in chloroform at 30°C; made by Mitsubishi Petrochemical Co., Ltd.),
- 10 Polystyrene (HF-77, a product of Mitsubish Monsanto Co., Ltd.),
- Maleic anhydride-grafted ethylene-propylene copolymer (containing 1.5 wt% of maleic anhydride; made by Mitsubishi Petrochemical Co., Ltd.),
- 15 Styrene-butadiene copolymer (1502, a product of Japan Synthetic Rubber Co., Ltd.),
- Precipitated calcium carbonate (average particle diameter 0.2 micron),
- Triphenyl phosphate (flame retardant), and
- 20 N,N'-diphenyladipic acid diamide.

The resulting pellets were injection-molded at a temperature of 300°C under an injection pressure of 1100 kg/cm² by using an injection-molding machine N-100 (made by The Japan Steel Works, Ltd.) to measure the

25 flow distance in a spiral cavity, 12 mm thick and 8 mm wide. Test pieces were formed by using the same injec-

- 35 -

tion molding machine as above, for evaluating the flame retardance according to UL Standards, Subject 94.

In Comparative Example, the same experiments as in
5 Example were carried out except that N,N'-diphenyladipic
acid diamide was not used. The results are shown in
Table 7. These results suggest that the addition of
N,N'-diphenyladipic acid diamide greatly improves the
flowability of the composition without any adverse
10 effect on flame retardance.

- 36 -

Table 7

| | <u>Example</u> | <u>Comparative Example</u> |
|--|----------------|--------------------------------|
| | <u>29</u> | <u>17</u> |
| <u>Formulation</u> (parts by weight) | | |
| Poly-2,6-dimethyl-1,4-phenylene ether | 45 | 45 |
| Polystyrene | 45 | 45 |
| Maleic anhydride-grafted ethylene-propylene copolymer | 5 | 5 |
| Styrene-butadiene copolymer | 5 | 5 |
| Calcium carbonate | 5 | 5 |
| Triphenyl phosphate | 8 | 8 |
| N,N'-diphenyladipic acid diamide | 5 | - |
| <u>Performance</u> | | |
| Spiral flow distance (mm) | 522 | 390 |
| Flame retardance according to UL-94 (1.59 mm thick specimen) | 94V-1 | 94V-1 |

- 37 -

EXAMPLE 30 and COMPARATIVE EXAMPLE 18

The following components were uniformly blended in the ratio shown in Table 8 by using a supermixer, and
5 then mixed at 280°C and pelletized by using a twin-screw extruder (PCM-45ø) made by Ikegai Iron Works, Ltd. Poly-2,6-dimethyl-1,4-phenylene ether (having an intrinsic viscosity of 0.45 measured in chloroform at 30°C; made by Mitsubishi Petrochemical Co., Ltd.),
10 Polystyrene (HF-77, a product of Mitsubish Monsanto Co., Ltd.), Maleic anhydride-grafted ethylene-propylene copolymer (containing 1.5 wt% of maleic anhydride; made by Mitsubishi Petrochemical Co., Ltd.),
15 Styrene-butadiene copolymer (1502, a product of Japan Synthetic Rubber Co., Ltd.), Precipitated calcium carbonate (average particle diameter 0.2 micron),
2,6,7-trioxa-1-phosphobicyclo[2,2,2]octane-4-ethyl-1-oxide
20 (flame retardant), and N,N'-diphenyladipic acid diamide.

The resulting pellets were injection-molded at a temperature of 300°C under an injection pressure of 1100 kg/cm² by using an injection molding machine N-100
25 (made by The Japan Steel Works, Ltd.) to measure the flow distance in a spiral cavity, 2 mm thick and 8 mm

- 38 -

wide. Test pieces were formed by using the same injection molding machine as above, for evaluating the flame retardance according to UL Standards, Subject 94.

- 5 In Comparative Example, the same experiments as in Example were carried out except that N,N'-diphenyladipic acid diamide was not used. The results are shown in Table 8. These results suggest that the addition of N,N'-diphenyladipic acid diamide greatly improves the
- 10 flowability of the composition without any adverse effect on flame retardance.

- 39 -

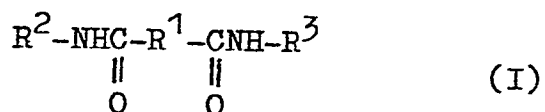
Table 8

| | <u>Example</u> | <u>Comparative Example</u> |
|--|----------------|--------------------------------|
| | <u>30</u> | <u>18</u> |
| <u>Formulation (parts by weight)</u> | | |
| Poly-2,6-dimethyl-1,4-phenylene ether | 65 | 65 |
| Polystyrene | 25 | 25 |
| Maleic anhydride-grafted ethylene-propylene copolymer | 5 | 5 |
| Styrene-butadiene copolymer | 5 | 5 |
| Calcium carbonate | 5 | 5 |
| 2,6,7-trioxa-1-phospho-bicyclo[2,2,2]octane-4-ethyl | 5 | 5 |
| N,N'-diphenyladipic acid diamide | 6 | - |
| <u>Performance</u> | | |
| Spiral flow distance (mm) | 295 | 203 |
| Flame retardance according to UL-94 (1.59 mm thick specimen) | 94V-1 | 94V-1 |

- 40 -

CLAIMS:

1. A polyphenylene ether composition having improved processability comprising a polyphenylene ether
 5 and an additive characterised in that the additive is a diamide compound represented by the following general formula (I):-



- wherein R^1 is a C_{1-10} linear or branched saturated or
 10 unsaturated aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue, an aromatic hydrocarbon residue, or such a residue having one or more substituents; and R^2 and R^3 , which may be the same or different, are each a C_{1-10} linear or branched saturated or unsaturated
 15 aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue or an aromatic hydrocarbon residue, or such a residue having one or more substituents.

2. A composition as claimed in Claim 1, wherein the diamide compound (I) has a melting point of 105°C
 20 or higher.

3. A composition as claimed in Claim 1 or 2, wherein the amount of the diamide compound (I) is 0.1 to 25 parts per 100 parts of total polymer, by weight.

4. A composition as claimed in Claim 3, wherein
 25 the amount of the diamide compound (I) is 2 to 10 parts

per 100 parts of total polymer by weight.

5. A composition as claimed in any preceding claim, wherein R^2 and R^3 in the general formula (I)

5 are each an unsubstituted phenyl or substituted phenyl group and the diamide compound has a melting point of 130°C or higher.

6. A composition as claimed in any preceding claim, wherein a styrene resin is present in an amount
10 of up to 2,000 parts per 100 parts of polyphenylene ether by weight.

7. A composition as claimed in Claim 6, wherein the styrene resin is a rubber-modified polystyrene resin.

8. A composition as claimed in Claim 6 or 7,
15 wherein a rubbery polymer is present in an amount of 0.5 to 50 wt% based on the total weight of polymer.

9. A composition as claimed in Claim 8, wherein an inorganic filler is present in an amount of 0.5 to 60 wt% based on the weight of the composition.

20 10. A composition as claimed in Claim 6 or 7, wherein there is present a polystyrene-grafted polyolefin in an amount of 1 to 80 wt% based on the total weight polymer and/or a polyphenylene ether-grafted polyolefin in an amount of 1 to 50wt% based on the total weight of
25 polymer.

1/3

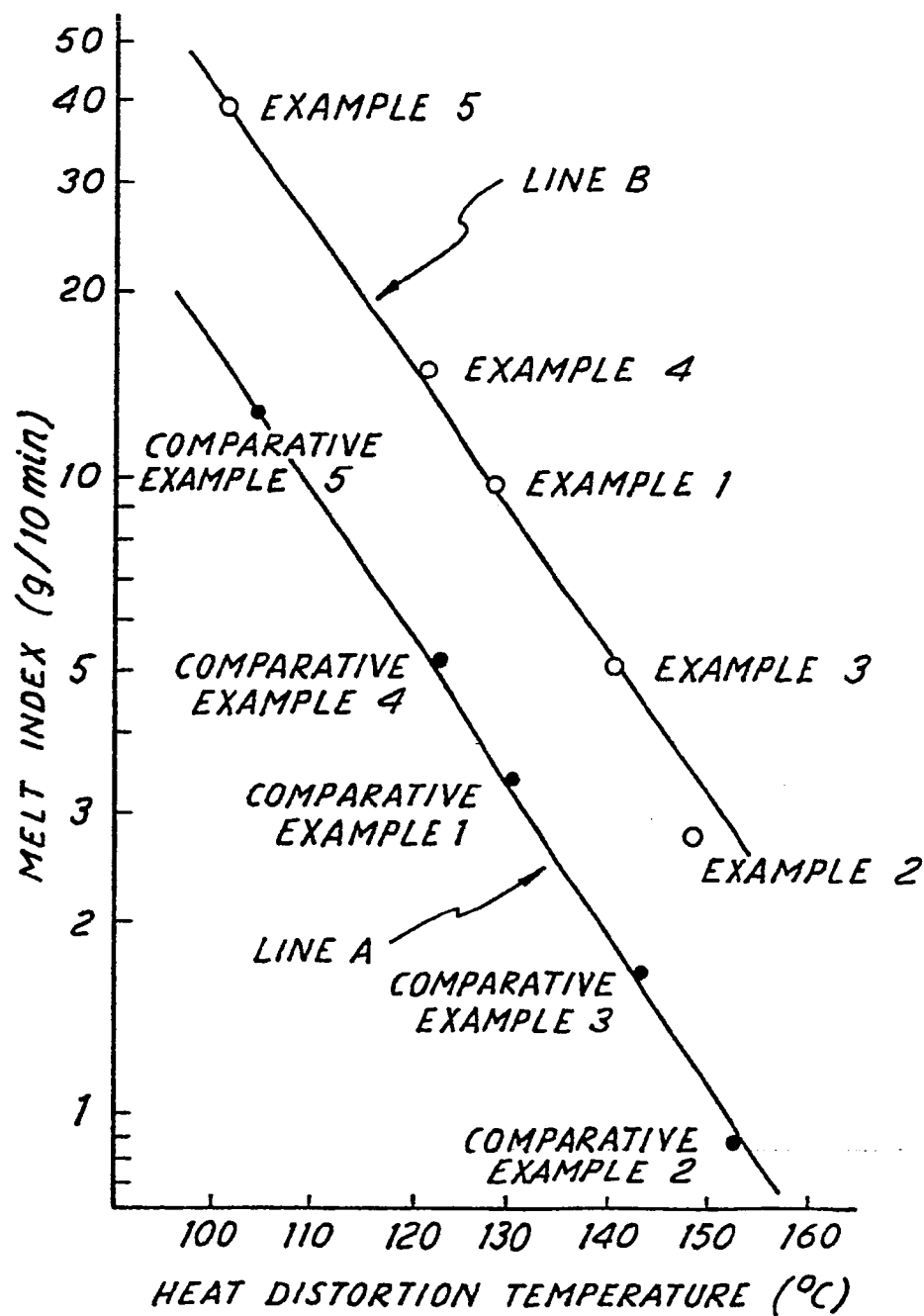


FIG. 1

2/3

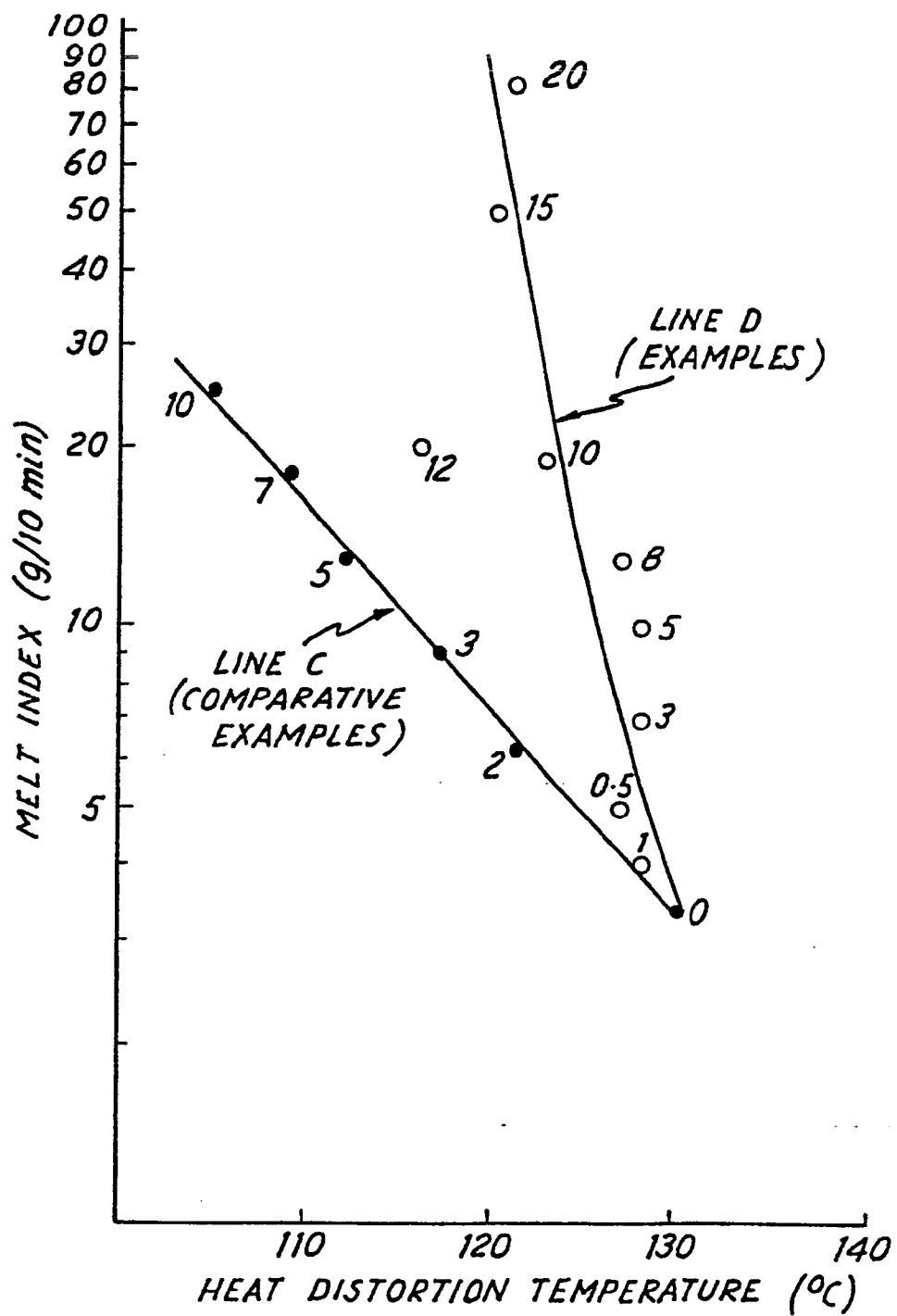
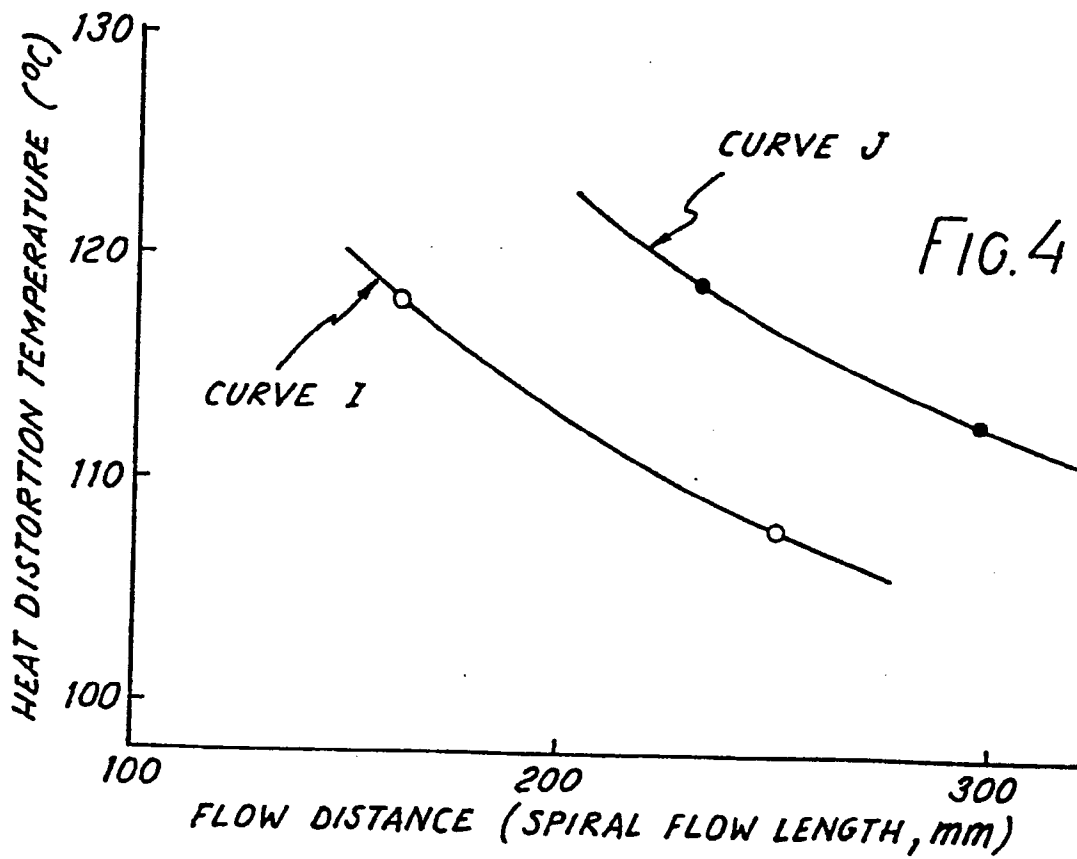
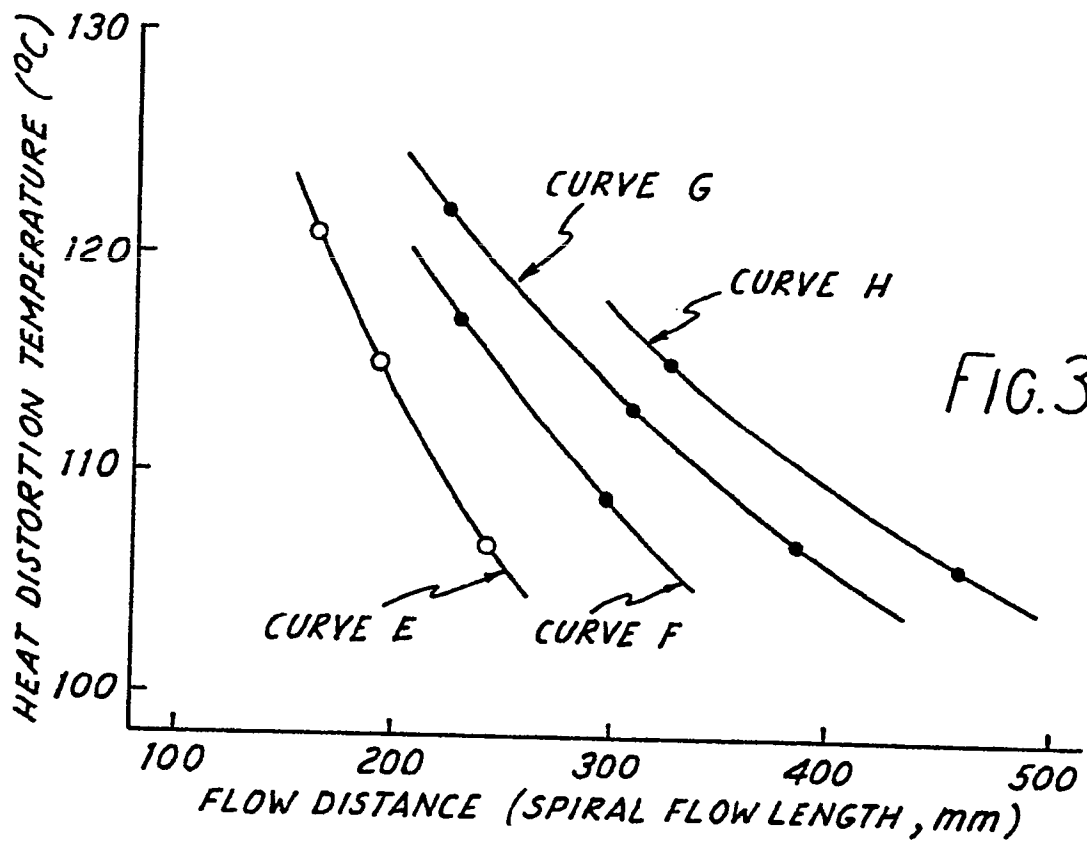


FIG. 2

3/3



(12)

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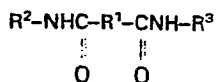
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(54) **Polyphenylene ether compositions having improved processability.**

(57) A polyphenylene ether composition comprises polyphenylene ether, optionally styrene resin, and a diamide represented by the formula



wherein R¹ is a C₁₋₁₀ linear or branched saturated or unsaturated aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue, an aromatic hydrocarbon residue, or such a residue having one or more substituents; and R² and R³, which may be the same or different, are each a C₁₋₁₀ linear or branched saturated or unsaturated aliphatic hydrocarbon residue, an alicyclic hydrocarbon residue or an aromatic hydrocarbon residue, or such a residue having one or more substituents.

The composition has improved processability, due to high flowability, with a minimum decrease in heat resistance.



| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|--|--|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int. Cl. 3) |
| A | US-A-3 956 423 (A. KATCHMAN) * claims 1, 3, 4 * | 1, 3, 4, 6, 7, 9 | C 08 L 71/04 C 08 L 25/10 C 08 K 5/20 |
| A | US-A-2 683 132 (D.W. YOUNG et al.) * claims 1, 3, 5, 8; column 5, lines 56-67; column 6, line 63 - column 7, line 2 * | 1, 5-7 | |
| A | DE-A-2 018 716 (CIBA) * claims 1-9, page 5, lines 17-23 * | 1, 3-7 | |
| A | PATENT ABSTRACTS OF JAPAN, vol. 4, no. 77 (C-13)[559], 4th June 1980; & JP - A - 55 40781 (MITSUBISHI KASEI KOGYO K.K.) 23-03-1980 | 1, 3 | |
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| The present search report has been drawn up for all claims | | | TECHNICAL FIELDS SEARCHED (Int. Cl. 3) C 08 L 71/00 C 08 L 25/00 C 08 K 5/00 |
| Place of search BERLIN | | Date of completion of the search 20-02-1987 | Examiner BOEKER R.B. |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | | | |